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SOME QUESTIONS ON THE FORMATION OF CORROSIVE SULFUR AND VANADIUM COMPOUNDS CONTAINED IN FUEL OILS DURING BURNING IN GAS TURBINE POWER PLANT COMBUSTION CHAMBERS

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SOME QUESTIONS ON THE FORMATION OF CORROSIVE SULFUR AND VANADIUM COMPOUNDS CONTAINED IN FUEL OILS DURING BURNING IN GAS TURBINE POWER PLANT COMBUSTION CHAMBERS

[Nekotorye voprosy obrazovaniya korrozionnoagressivnykh coedineniy sery i vanadiya, soderzhashchikhsya v neftyanykh toplivakh, pri gorenii v kamerakh sgoraniya GTU]

by

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Mastering the combustion of liquid fuels which are in abundant supply (mazut and distillates of delayed coking) in stationary gas turbine power plants (GTU) is an important national economic task on whose solution depend the prospects for employing the GTU in power engineering and industry.

The combustion of heavy liquid fuels is related to the solution of an entire range of problems which do not occur in the operation of the GTU on natural gas or disel fuel. This is primarily a problem of ash deposits and corrosion of the metal surfaces in the ducts of the gas turbine power

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plants. The presence of sulfur in the fuel results in the formation of sulfuric anhydride SO_3 in the combustion products; as a consequence, the dew point of the flue gases increases considerably and sulfuric acid corrosion occurs on the low-temperature surfaces of the gas turbine power plant. The combined action of the vanadium and sodium compounds to a considerable degree determines the metal corrosion and the formation of ash deposits in the flow-through portion of the gas turbines.

According to the mechanism involved in the homogeneous formation of SO_3 in the combustion of sulfurous fuels [1], two reactions take place in the high temperature zone:

I--rapid oxidation of SO_2 by atomic oxygen;

II--slow dissociation of the forming SO_3.

Thus, a consecutive reaction occurs in the following manner:

$$SO_2 + O \xrightarrow{K_1} SO_3 \xrightarrow{K_2} SO_2 + \tfrac{1}{2}O_2 ,$$

where K_1 and K_2 are the rate constants for reactions I and II; $K_1 > K_2$.

Both of these reactions, with sufficient approximation, can be considered as first order reactions. Then the maximum possible concentration of SO_3 for the given conditions and the time needed to reach it are determined according to the formulas:

$$SO_{3\,MAX} = a\left(\frac{K_2}{K_1}\right)^{\frac{K_2}{K_1-K_2}},$$

$$\tau_{MAX.CONC.} = \frac{1}{K_1-K_2}\ln\frac{K_1}{K_2},$$

where a is the initial concentration of atomic oxygen.

On the basis of an analysis of the data [1-3], a curve was constructed

for the dependence of SO_3 formation on the coefficient of excess air in the combustion zone (fig. 1). Certain underlying and calculated data employed in the construction of this relationship are presented in the table.

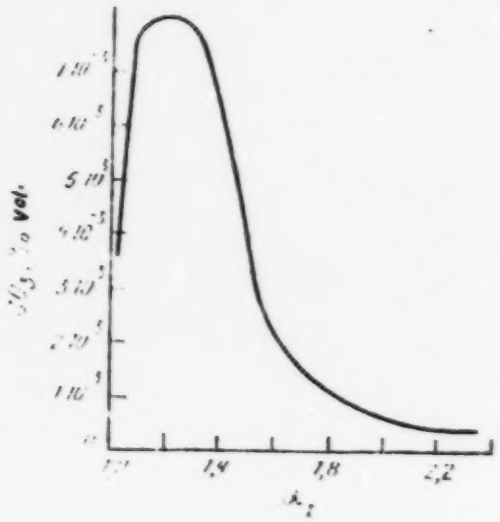

Fig. 1. Dependence of SO_3 content in combustion products on excess air in combustion zone.

Underlying and calculated data for construction of dependence of SO_3 formation on coefficient of excess air in the combustion zone*

Name	Combustion temperature, °K			
	1813	1783	1355	1260
SO_2 init., mole/cm³		$8.75 \cdot 10^{-8}$		
$O_{init.}$, % volum.	0.01	0.00535	0.00070	0.00035
K_1, sec^{-1}	100	97.3	57.1	48.4
K_2, sec^{-1}	16.3	14.1	0.783	0.317
SO_3 max, % volum.	$7 \cdot 10^{-3}$	$3.85 \cdot 10^{-3}$	$0.66 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$
τ max. conc., sec.	0.022	0.023	0.076	0.105

*Pressure--atmospheric

The calculated formulas for the rate constants K_1 and K_2 have been obtained in the following manner. The common form for the calculated formulas accepted as

$$K = \varkappa e^{-\frac{E}{RT}}$$

where E is the activation energy;

T is the absolute temperature of the reaction.

For reaction I

$$\varkappa = \varkappa SO_2 \text{ init.},$$

where SO_2 init. is the original concentration of SO_2.

According to the experimental data [1,3], at a temperature of roughly 1500°C, $\varkappa^1 = 1.1 \cdot 10^9 cm^3/mole \cdot sec.$, $K_2 = 11.6$ sec.$^{-1}$.

The activation energy of the reaction

$$SO_2 + O \rightarrow SO_3$$

is accepted as equal to 6000 cal/mole, while for the reaction

$$SO_2 + \tfrac{1}{2}O_2 \longrightarrow SO_3$$

is equal to 10,000 cal/mole [2]. The equilibrium constant of reaction $SO_2 + \frac{1}{2}O_2 \rightleftarrows SO_3$ is

$$K_p = 2.3 \cdot 10^{-5} e^{\frac{22600}{RT}}.$$

Thus,

$$K_1 = 6 \cdot 10^9 e^{-\frac{6000}{RT}} \cdot SO_2 \text{ init.} \quad [\text{sec.}^{-1}], \qquad (3)$$

$$K_2 = 1.3 \cdot 10^5 e^{-\frac{32600}{RT}} \quad [\text{sec.}^{-1}]. \qquad (4)$$

The curve (fig. 1) shows that there is a certain area of values α_1 which is optimal for the formation of SO_2 (for the conditions accepted as the initial ones in the construction of fig. 1, $\alpha_1 \approx 1.1 - 1.4$). With

α_1 (illegible) 1.1 the formation of SO_3 is impeded due to the low content of oxygen in the combustion zone. With values of α_1 (illegible) 1.4 the rate of SO_3 formation is reduced due to a drop in the temperature level of the fuel spray.

Currently, water heaters have been successfully employed in which the fuel is burned with small excesses of air (α_1 (illegible) 1.02 - 1.06) which permits an efficient reduction in SO_3 formation and consequently, a reduction in the corrosion of the "tail" surfaces.

The combustion patterns in the GTU combustion chambers are essentially different from the patterns in furnaces of water heaters and other furnace units. Special features in the operation of the GTU combustion chambers include increased pressures in the combustion zone, considerable heat stresses in the furnace space and also large air excesses.

We established the goal of determining by a calculation method the effect of the conditions involved in fuel combustion in the gas turbine power plant (GTU) on the mechanism of homogeneous formation of SO_3, in particular, on the ratios of the orders of SO_3 formation rates during SO_2 oxidation by atomic and molecular oxygen.

For combustion chambers of stationary gas turbine power plants operating on a calculated pattern with α_1 = 1.3 -2.0 and the volume heat stress q_v = 3-5 Mw/m^3 · bar, the time the combustion products remain in the furnace space of the combustion chamber is equal to 0.035 - 0.06 sec.

It is apparent from the table that while the combustion products are in the high-temperature zones the formation of considerable concentrations of SO_3 is possible.

Fig. 2 presents the dependence of SO_3 formation on pressure according

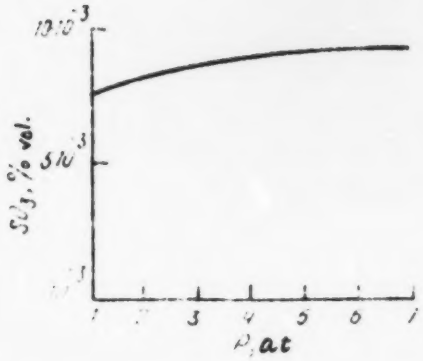

Fig. 2. Dependence of SO_3 formation on pressure according to the reaction $SO_2 + O \rightarrow SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$
$SO_{2_{init}} = 0.11\%$ volum; $O_{init} = 0.01\%$ volum; $t \approx 1500°C$.

to the reaction

$$SO_2 + O \rightarrow SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2$$

with temperature~1500°C. Underlying data are taken from [1]. Taking into consideration that the rate constants K_1 and K_2 depend only on temperature, from expression (1) we obtain the formula for computing the curve in fig. 2:

$$SO_{3_{max}} = a(\beta \cdot p)\frac{1}{1 - \beta p},$$

where a and β are constant at the given temperature;

p is the pressure in the reaction space.

Fig. 2 indicates that with an increase in pressure there is a greater SO_3 formation.

The calculations made by the authors show that the operating conditions for the combustion chambers of the stationary gas turbine power plants are favorable for the formation of sulfuric anhydride during the oxidation of SO_2 by atomic oxygen.

Oxidation of SO_2 by molecular oxygen is a third order reaction. The

rate of SO_3 formation in this reaction is described by the differential equation:

$$\frac{dSO_3}{d\tau} = K(a - SO_3)^2\left(\beta - \frac{SO_3}{2}\right) - K_2 (SO_3)^2,$$

where a and β is the initial concentration of SO_2 and O_2 respectively;

SO_3 is the concentration of SO_3 with the lapse of time τ after the beginning of the reaction;

K is the rate constant of reaction

$$2SO_2 + O_2 \rightarrow 2SO_3;$$

K_2 is the rate constant of reaction

$$2SO_3 \rightarrow 2SO_2 + O_2.$$

This equation can be simplified with sufficient accuracy. Since the fuel is burned in combustion chambers of the GTU with great air excesses and the oxygen concentrations in the combustion products are considerably higher than the concentrations of SO_3, then

$$\frac{dSO_3}{d\tau} = K(a - SO_3)^2 \beta - K_2 (SO_3)^2.$$

From this equation, supplying the value

$$K_2 = K \frac{(a - SO_{3\,equil})^2 \beta}{SO_{3\,equil}^2},$$

we obtain the expression for determining the actual SO_3 concentration:

$$SO_3 = \frac{a\, SO_{3\,equil}\,(e^{a\tau} - 1)}{a(e^{a\tau} + 1) - 2 \cdot SO_{3\,equil}},$$

where

$$A = \frac{2K \cdot a \cdot \beta (a - SO_{3\,equil.})}{SO_{3\,equil.}};$$

$SO_{3\ equil}$ is the SO_3 concentration at the reaction equilibrium.

Fig. 3 (a, b) presents the dependence of SO_3 formation in the reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

on the temperature and pressure; the time τ which the combustion products spend in the gas duct of the GTU is accepted as equal to 4 sec.

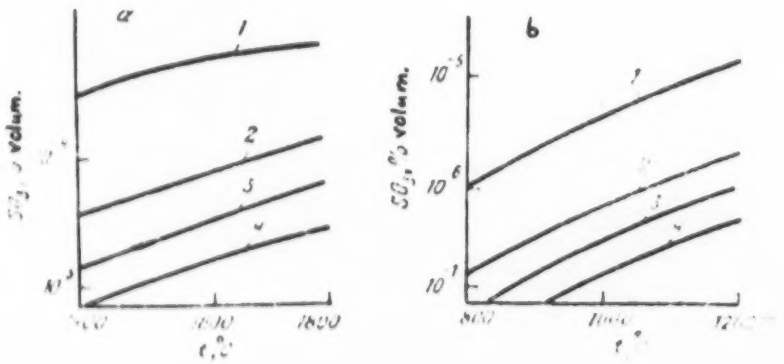

Fig. 3. Dependence of SO_3 formation in the reaction $2SO_2 + O_2 \rightleftarrows 2SO_3$ on pressure and temperature (reaction time τ = 4 sec);
a--α = 1.5; b--α = 7; 1,2,3,4--25, 10, 7, 5 at. respectively.

By comparing fig. 2 and 3 one can see that while the combustion products are in the GTU gas duct, sulfuric anhydride in practice is not formed in the reaction of SO_2 with molecular oxygen; the primary factor in the homogeneous formation of SO_3 in the GTU is the interaction of SO_2 with atomic oxygen.

In fuel combustion, vanadium passes into the combustion products

mainly in the form of V_2O_3, as well as in certain amounts in the form of V_2O_4. The formation of V_2O_3 occurs during the thermal splitting of vanadium-porphyrine complexes in which two atoms of vanadium are bonded with three atoms of oxygen; V_2O_4 formation, apparently, occurs during the thermal splitting of other vanadium-containing organic fuel compounds.

V_2O_3 and V_2O_4 have a high melting temperature (1970 and 1967°C respectively) and a very low vapor pressure, therefore these oxides remain solid at the temperatures of the combustion products.

In the environment of excess oxygen in the air, V_2O_3 and V_2O_4 are oxidized to V_2O_5. The pressure of the saturating V_2O_5 vapors increases sharply when the temperature is over 1200°C. As the temperature of the flow drops in the gas duct of the gas turbine power plant the partial pressure of the V_2O_5 can be higher than the pressure of the saturating V_2O_5 vapors at the same temperature; in this case, the vapors of vanadium pentoxide will condense.

Preliminary experiments conducted at the F. E. Dzershinskiy All-Union Heat Engineering Institute have shown that by creating the appropriate pattern conditions in the combustion zone one can affect the ash deposits and corrosion of the flow-through section of the GTU without changing the volume heat stresses and without altering the organization principle of the combustion process. Based on the thermodynamics and kinetics of the formation of corrosive compounds of SO_3 and V_2O_5, in order to prevent the formation of these compounds in the GTU combustion chamber it is necessary to decrease the time which the combustion products spend in the high-temperature zones (1500-1800°C) and then drastically cool the combustion products to a temperature of 1000-1100°C. These conditions

. . . .

are met by implementing the process of combustion of liquid fuels with a coefficient of air excess, supplied for the fuel combustion, equal to 1.6-2.0 and with the creation of an effective mixture in the anterior zone of the combustion chamber.

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